

Methanesulfonic Acid-Catalyzed Additions IV

Additions to Methyl Linoleate¹

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Abstract

Varied aromatic compounds including phenol, *o*-chlorophenol, 2-naphthol, resorcinol, methyl salicylate, anisole, phenetole, *p*-toluenethiol, *p*-chlorobenzenethiol and 2-naphthalenethiol were added to methyl linoleate. Using methanesulfonic acid as a solvent-catalyst the additions took place as readily as to oleic acid in previous experiments. The recovery of mono-adducts, however, was complicated by the presence of di-adducts and presumably polymeric material.

As observed in the earlier oleic acid studies, evidence for the formation of ether intermediates was obtained. The only identified products from arylthiol additions were thioethers.

Introduction

METHANESULFONIC ACID, like H_2SO_4 , has a hydrogen bonded structure, high dielectric constant and, although weaker than H_2SO_4 , has high proton availability (1). It does not have the tendency to oxidize organic compounds as readily as H_2SO_4 . This latter property suggested its possibilities as a substitute for H_2SO_4 as a carbonium ion producer and catalyst for addition reactions. Recent reports from this laboratory (2,3,4) have described the acid-catalyzed addition of phenols, arylthiols, phenyl ethers and benzoic acid to oleic acid and to cyclohexene with methanesulfonic acid playing the role of both solvent and catalyst for the reaction. It was particularly noteworthy that arylthiols could be added in this medium since previous investigators (5) experienced difficulties with this reaction when sulfuric acid was used.

This report concerns the investigation of the addition reaction directed toward linoleic acid as its methyl ester. In this case, both mono-addition and di-addition products are possible. A number of the nucleophilic substances that were successfully added to oleic acid and to cyclohexene were tried similarly with methyl linoleate. In most instances good yields of products were obtained but the recovery of the products was more involved. Methyl linoleate, a more reactive compound than oleic acid, had a greater tendency to form polyaddition products and polymeric substances. The presence of these materials complicated the separation procedures. The results of the addition experiments are summarized in Table I.

In an earlier communication (3), it was noted that previous investigators, particularly Niederl et al. (6, 7,8), had proposed a mechanism for the addition of a phenol to an olefin which involved the formation of an ether intermediate which subsequently rearranged to form the final product. Evidence supporting this mechanism was obtained by us from an IR study of fractions resulting from the methanesulfonic acid-catalyzed addition of *m*-cresol to oleic acid.

A similar type of evidence was obtained by IR examination of the product obtained from the methanesulfonic acid-catalyzed addition of 2-naphthol to methyl linoleate. The crude product showed a high degree of absorption at 1250 cm^{-1} characteristic of arylalkyl ethers, and absorption present in the $3300\text{--}3700\text{ cm}^{-1}$ region indicated the presence of free hydroxyl groups. These findings suggested that the product contained a mixture of both 2-naphthoxy and hydroxynaphthyl derivatives. Both of the characteristic absorptions were present in the spectra of the early fractions obtained from molecular distillation of the crude product. This indicated that other means were necessary to effect the separation. As expected, the analyses of these fractions agreed well with theory for a mono-addition product in all respects except for hydroxyl content.

By adoption of the procedures found to be successful in our earlier work on oleic acid, it was possible to effect a separation by chromatography. The 2-naphthoxy derivative is less polar than the derivative containing a free hydroxyl group, and the separation of the isomers was made by chromatography on a Florisil column. The early fractions eluted from the column when examined by IR had a strong absorption peak at 1250 cm^{-1} showing the presence of alkylaryl ether. The loss of absorption in the $3300\text{--}3700\text{ cm}^{-1}$ region indicated the absence of free hydroxyl groups. The fractions obtained from later elution with solvents of increased polarity showed hydroxyl absorption and a considerable lessening of the ether absorption.

Experimental

Starting Materials. Methyl linoleate (iodine value 169.8) was prepared by a method similar to that described by Parker et al. (9). This procedure involved the alcoholysis of safflower oil with methanol followed by urea separation and subsequent fractional vacuum distillation. The phenols, phenyl ethers and arylthiols were the best commercial grades available and were used without further purification.

Addition Reactions. All but one of the addition reactions were performed at room temp and in the

TABLE I
Addition Products of Methyl Linoleate

Compound added	Yield of molecularly distilled products	
	Mono-addition	Di-addition
	%	%
Phenol.....	52
2-Naphthol.....	44
<i>o</i> -Chlorophenol.....	49
Hydroquinone.....	Not distillable
Resorcinol.....	15
Methyl salicylate.....	38	20
<i>p</i> -Toluenethiol.....	32
2-Naphthalenethiol.....	15
<i>p</i> -Chlorobenzenethiol.....	10	27
Anisole.....	52	23
Phenetole.....	54	19

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² A laboratory of the E. Utiliz. Res. & Dev. Div., ARS, USDA.

same manner as that described in our previous publications. The addition of methyl salicylate was carried out at 50–60°C. In general, the procedure consisted in slowly adding, with good stirring, methanesulfonic acid to the mixture of the phenol (or phenyl ether or arylthiol) and methyl linoleate. The molar ratios of reactants were: 6 moles methanesulfonic acid to 4 moles phenol to 1 mole methyl linoleate. After six hr the reaction mixture was poured onto cracked ice. The crude product was isolated by extraction with ether. After ether removal the crude products were then subjected to molecular distillation in a rotating falling film molecular still.

Chromatography. Florisil was used as the adsorbent for the chromatographic separation of the 2-naphthoxy and hydroxynaphthyl compounds obtained in the 2-naphthol addition experiments. A 30:1 ratio of adsorbent to material was employed to effect the separation. Elution with hexane removed the 2-naphthoxy derivative. By increasing the polarity of the eluting solvent by adding benzene to the hexane (20% benzene–80% hexane), the hydroxynaphthyl compound was removed from the column. There was ca. a 1:1 ratio of ether to hydroxy compound.

Discussion

The yield data reported in Table I for the distillate fractions were obtained by comparing the analyses of the fractions from the molecular distillation with the theoretical values for mono-addition and di-addition products.

The addition of phenol yielded a molecularly distilled product which had the following analysis:

Carbon %		Hydrogen %		OH %		S. E.	
Calc. for mono-addn.	Found	Calc.	Found	Calc.	Found	Calc.	Found
77.27	77.00	10.38	10.11	4.23	4.36	389	401

Mol Wt Calc. 389; Found 386 [Thermo-electric Method (10)].

Theory for di-addition products S. E. and mol wt—482 and OH% 7.05. Inspection of the analytical data indicates that the product is a mono-addition product.

TABLE II

Analyses of *p*-Chlorobenzenethiol—Methyl Linoleate Addition Products

	Calc. for mono-addn.	Calc. for di-addn.	Found		
			Fraction 1	Fraction 2	Fraction 3
% Carbon	68.38	63.78	66.95	64.74	63.84
% Hydrogen	8.95	7.60	8.72	7.81	7.59
% Chlorine	8.08	12.15	9.03	11.06	12.14
% Sulfur	7.30	10.99	7.98	9.89	10.86
Mol wt	439	504	474	542	579

In the case of addition of *p*-chlorobenzenethiol, the analyses of three fractions obtained by molecular distillation are listed in Table II. The data indicate that Fraction 1 (10%) is comprised primarily of mono-addition product. Fraction 2 is mostly di-addition product with a small amt of mono-addition product. Fraction 3 is primarily di-addition product. Collectively, about a 27% yield of di-addition product was obtained.

Phenyl ethers such as phenetole added to methyl linoleate very readily. The two main fractions obtained had the following analyses:

a) 49% mono-addition product:

Carbon %		Hydrogen %		S. E.	
Calc.	Found	Calc.	Found	Calc.	Found
77.83	77.96	10.65	10.54	416	420

Mol Wt Calc. 416; Found 390 (10).

b) 14% di-addition product:

Carbon %		Hydrogen %		S. E.	
Calc.	Found	Calc.	Found	Calc.	Found
78.01	77.96	10.10	10.13	538	506

Mol Wt Calc. 538; Found 499 (10).

An intermediate fraction (9%) comprising a mixture of mono- and di-addition products was also obtained.

The recovery of addition products of methyl linoleate was hampered by the presence of high mol wt polymeric products, especially in the experiments using hydroquinone and resorcinol as the phenolic nucleophiles. In experiments involving *p*-chlorobenzenethiol and 2-naphthalenethiol, ether-insoluble products were obtained. These results were contrary to our normal experience. A further examination, by chromatography, of the ether-insoluble product from the 2-naphthalenethiol experiment revealed it to be a mixture of the 2-naphthalenethiol addition product to free linoleic acid and as yet an unidentified material.

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